CHAPTER–(3)

THEORETICAL CONSIDERATIONS

CHAPTER – 3

THEORETICAL CONSIDERATIONS

3.0.0 VARIOUS ASPECTS CONSIDERED UNDER HEADING "THEORETICAL CONSIDERATIONS"

Theoretical considerations for quaternary phase equilibrium data which can be converted to equivalent Ternary phase equilibrium data using concept of dual solvent- (solvent + anti solvent) - have been outlined with respect to following:–

(i). Mutual solubility data and Tie - line data inclusive of plait point.
(ii). Distribution curves diagrams and selectivity diagrams.
(iii). Tie line data correlations.
(iv). Quaternary tie line data correlations based concept of equivalent ternary phase equilibrium data.
(v). Unifac model, uniquac model and NRTL equations.

Theoretical considerations for liquid – liquid extraction in a packed column have been also outlined with respect to following -

(i). Hold up of dispersed phase
(ii). % aromatics extracted and % purity of extract.
(iii). Mass transfer aspects like NTU, HTU, Kodxa and Kocxa inclusive of determing these values.

All relevant necessary equations have been outlined in this chapter and these equations have been used subsequently while preparing data processing tables.

3.1.0 Theoretical considerations for Phase equilibrium data:

3.1.1Ternary phase liquid equilibrium:

Representation of ternary phase equilibrium data, estimation of plait point and construction ofDistributuion diagramshave been outlined in following paragraphs.

(i) Distribution curves:

The equilibrium data can also be represented by a distribution curve[131] obtained by plotting the equilibrium composition of the solute in the solvent-rich phase against the equilibrium composition of the solute in the diluents-rich phase, as shown in Fig.1 The slope of the equilibrium distribution curve thus obtained gives the value of the distribution coefficient, m, at any location on the curve.

(ii)Other method of Representing Equilibrium Data:

The other method of representing equilibrium data is by Right angle Triangular Diagram[131] as shown in Fig. 2

Fractions of solvent in both phases are plotted against the concentration of solute in both phases, on solvent- free basis. In the method shown in Fig. 1 concentration of solute in the conjugate phases at equilibrium is plotted on solute-free parameters: this method is often used for systems in which the solvent and diluents are completely immiscible.

(iii)Estimation of plait point

Plait point[131] in the ternary systems indicates the maximum concentration of the solute in the raffinate phases that can possibly be handled in any extraction system . Various methods are available for the estimation of this plait point. The conjugate curve method Fig. 3 is used for the determination of the plait point composition.

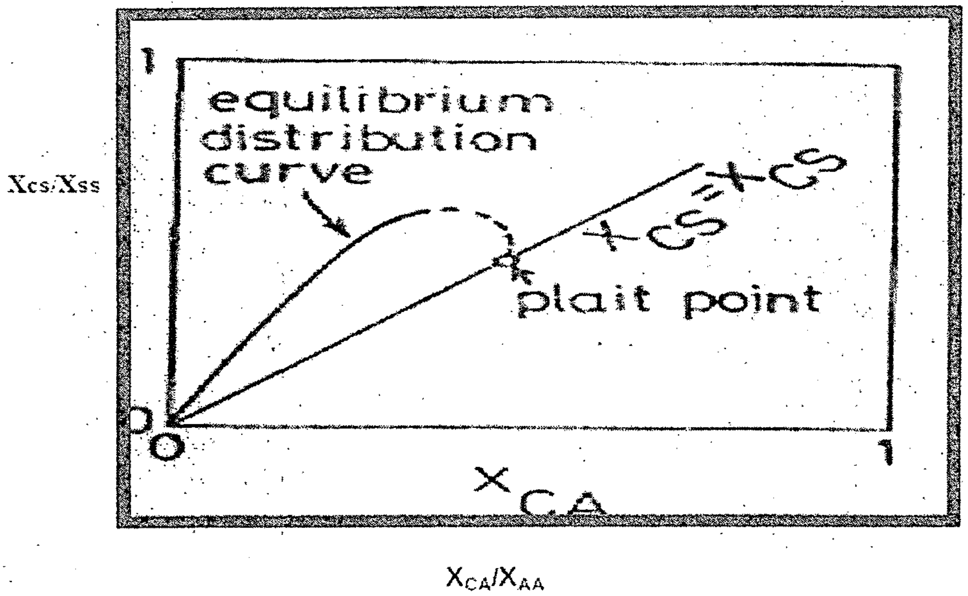

Fig...1 The slope of the equilibrium distribution curve

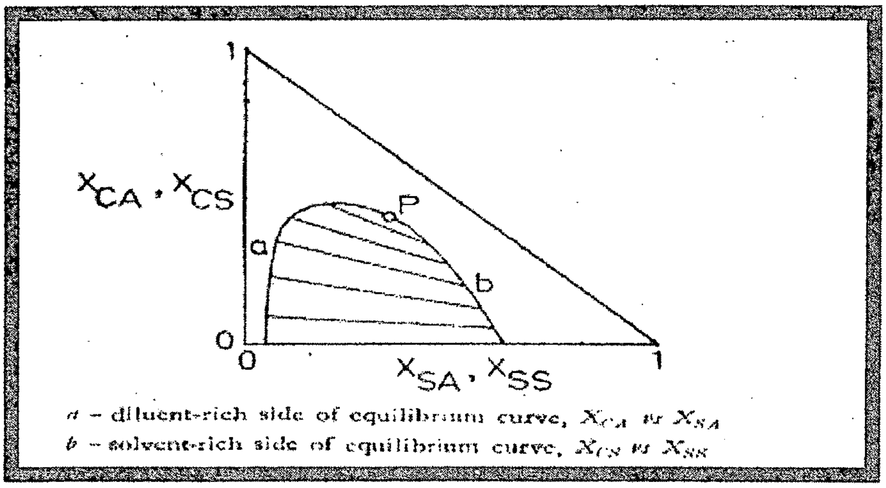

Fig. 2 Right angle Triangular Diagram

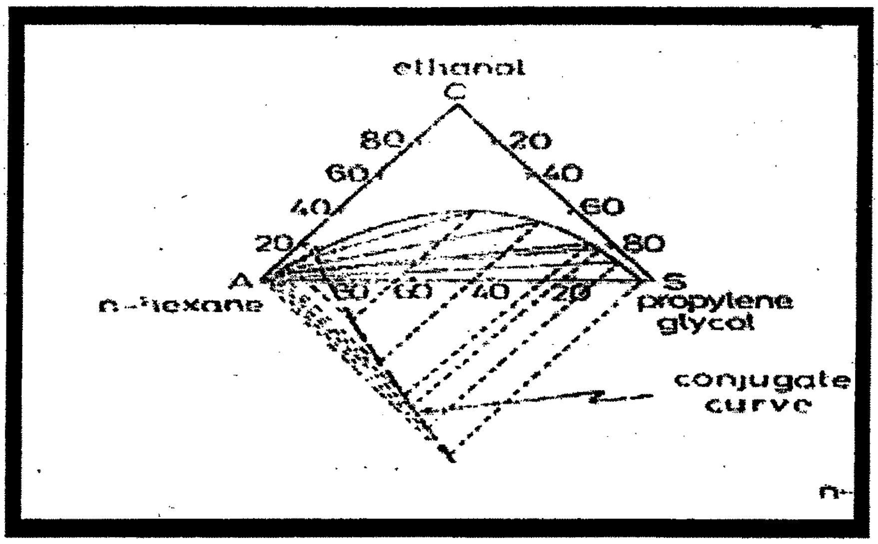

Fig. 3 The determination of the plait point composition

3.1.2 Various methods for the Tie line Equilibrium data correlation:

The following are the four important methods available in the literature for correlating Tie line data:

1) Hand's method
2) Campbell 's method
3) Bachman's method
4) Othmer and Tobias method

The relavant four correlations interms of mathematical equations are as under:

(i) Hand's correlation:

Hand's method[132] uses a double log arithmetic co-ordinate plot.

The data obtained could be correlated satisfactory by this method. Thus an equation of type may be given by: -

$[(X_{XE}) / (X_{SE} + X_{WE})] = (K) [X_{AR} / X_{A'R}]^{n}$ (1)

Where,

X_{AE} = wt.frac. of aromatic in Extract.

X_{SE} = wt.frac. of solvent in Extract phase.

X_{WE} = wt.frac. of water in Extract phase.

X_{AR} = wt.frac. of aromatic in raffinate.

$X_{A'R}$ = wt.frac. of aliphatic in raffinate.

K, n = Constants in Hand's correlation.

Thus if one plots a graph of log $X_{AR} / X_{A'R}$ vs. log $X_{AE}/X_{SE} + X_{WE}$ is expected to result in a straight line having intercept (log K) and slope (n).

(ii)Campbell's correlation:

Campbell has shown that a straight-line correlation results, when the concentrations of the solute in the conjugate phases are plotted on log-scale.

Campbell[133] has given the following equation

$C_1 = k_C (c_2)^{nc}$ (2)

Where,

C_1 = Weight fraction of solute in extract.

C_2 = Weight fraction of solute in raffinate.

K_c' n_c = Constants in Campbell's correlation.

(iii)Bachman's correlation:

Bachman's method[134] indicates that an equation of the following form is quite representative: -

$a_1 = n_B (a_1/b_2) + k_B)$ (3)

Where,

a_1 = Weight fraction of solvent in extract.

b2 = Weight fraction of non-solute in raffinate.

$k_B \cdot {}^n{}_B$ = Constants in Batechman's correlation.

(iv)Othmer and Tobias correlation:

Othmer and Tobias [135] equation as under:

$(1-a_1)/a_1 = k_{O.T.} [((1-b_2)/b_2)]^{n_{O.T.}}$ Where, (4)

a_1 = Weight fraction of solvent in extract.

b_2 = Weight fraction of non-solute in raffinate.

$k_{O.T}, n_{OT.}$ = Constants in Othmer and Tobias correlation.

3.1.3Quaternary Tie line data correlation base on Ternary data Correlation:

(i) Moulton and Chang's approach :

Moulton and Chang[13] have suggested a method of predicting the quaternary mutual solubility data from the basic ternary mutual solubility data. Quaternary system consisted of Ethyl alcohol -benzene-iso-valerate –water and corresponding two basic ternaries were-Ethyl alcohol –benzene-water andc Ethyl alcohol –Ethyl isovalerate-water The quaternary system Ethyl alcohol – benzene- iso- valerate – water has been studied on the basis of water in ethyl alcohol free ternary, equiratio ternary composition for the same water composition are found from the mutual solubility curves of two basic ternaries i.e. Ethyl- alcohol- benzene- water and Ethyl alcohol – Ethyl isovalerate – water, the difference between the ethyl alcohol and water composition .

It is than divided in the ratio of Benzene to ethyl isovalerate in original quaternary composition and is added to or subtracted from the corresponding equiratio values of Ethyl alcohol and water respectively. Remaining is then divided in benzene to Ethyl isovalerate ratio which completes the predicted quaternary composition. The predicted values are in good agreement with the original quaternary data.

(ii)Prince's Approach:

Prince[136]has given a generalized correlation for the double binary system i.e. system having pairs of particularly miscible liquids in the following formal .

$XAD/ XDD = [XAH/ (k1XBH + k2 XCH)]^{n1 - m (n1 - n2)}$ (5)

For the system A,B,C,D, where B-D and C-D are partially miscible pairs of liquids.H denotes the d poor phase and m the ratio

$m = XCH / [XCH + XBH]$

where XCH is the wt. fraction of C in H phase.n_1 and n_2 are the slopes of the basic ternaries in hand's plot . k_1 and k_2 are intercept for the same in the hand's plot .

(iii) Hand's approach applied to quaternary data-L-L extraction of aromatics:

According to Hand's correlation[137], for the ternary-benzene-Dmso-Water one can writs the following correlation:-

$[(X_{DE}) / (X_{BE})] = (K_1) [X_{DR} / X_{WR}]^{n}{}_{1}$ -----(3 .1)

Where,

X_{DE} = wt.frac. Of Dmf/ Dmso(solute) in Extract. phase.

X_{BE} = wt.frac. Of Benzene(solvent) in Extract phase.

.X_{DR} = wt.frac. Of Dmf/Dmso(solute) in raffinate. phase.

X_{WR} = wt.frac. Of water (non solute) in raffinate. phase.

Superimposing second ternary-Hexane- Dmf/Dmso-water, one can also write an equation similar to equation (1) follows:-

$[(X_{DE}) / (X^*_{BE})] = (K_1) [X_{DR} / X_{WR}]^{n1}$ ---------(3 . 2)

Where $X^*_{BE} = X_{HE} / (K_1/K_2) + X_{BE}$

Thus if one plots a graph of

Δ n=(n1+-n2) and log $X_{DE}/(K_1X_{BE} + K_2 X_{HE})$ Vs. n1log(X_{DR} / X_{BE}) .

Where $n1=(n_1-M_R.\ \Delta\ n)\ n_1$ and n_2 are the values of constants in the case of two basic ternaries namely-Benzene-Dmso-Water and Hexane-Dmso-water. Further

$M_R = (X_{HR} / X_{BR} + X_{HR})$--- (3.4) and $\Delta n = n_1 - n_2$ (since in the present case water acts as an anti-solvent,-ve sign has been used for n_2)

m=M/100=Wt.ester/(Wt ester+Wt.Benzene)

Thus, a plot of $(n_1 - M_R\ .\ \Delta\ n)$ log X_{DR} / X_{WR} Vs. log $X_{DE} /(K1\ X_{BE} + K_2\ X_{HE})$ is expected to be a straight line.

(iv)Modified Hand's equation applied to quaternary data:

Though the systems under consideration are quaternary in nature, if one considers a solvent as a dual solvent consisting of solvent + antisolvent, then all the systems under consideration can be reduced to ternary system. Data can be represented in terms X_{BE}, X_{HE}, and X_{SE} for Extract phase and X_{BR}, X_{HR} and X_{SR} for raffinate phase for a fixed concentration of antisolvent.

It has been observed that the values of equilibrium compositions in Extract phase and raffinate phase could be correlated in the form of an equation of type given by :-

$[(X_{XE})/(X_{SE}+X_{WE})]=(K)[X_{AR}/X_{A'R}]^n$ (7)

Where,

X_{AE} = wt.frac. of aromatic in Extract.

X_{SE} = wt.frac. of solvent in Extract phase.

X_{WE} = wt.frac. of water in Extract phase.

X_{AR} = wt.frac. of aromatic in raffinate.

$X_{A'R}$ = wt.frac. of aliphatic in raffinate.

Thus if one plots a graph of

log $[X_{AR} / X_{A'R}]$ vs. log $[(X_{AE})/(X_{SE} + X_{WE})]$

is expected to result in a straight line having intercept (logK) and slope (n) .

Thus quaternary L-L equilibrium data has been converted to pseudo ternary equilibrium data by treating solvent as dual solvent being Dmf/Dmso.+anti solvent water.

3.1.4 UNIFAC (UNIFAC FUNCTIONAL GROUP ACTIVITY COEFFICIENT) MODEL:

This is a group contribution method for prediction of activity coefficient in non-electrolyte liquid mixtures. The basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups which consistute these compounds is much smaller. Therefore if we assume that a physical property of a fluid is the sum of contribution made by the molecule's functional groups, we obtain a possible technique for correlating the properties of a very large number of fluids.In the UNIFAC method, originally presented by Fredenslund A. and Prausnitz J.M. (1975) [138]the combinatorial part of the UNIQUAC model i.e. eq (8) is used directly

$$\ln y_i^C = \ln(\varnothing_i / x_i) + z/2 * q_i \ln(\theta_i / \varnothing_i) + l_i - \varnothing_i / x_i \sum_{j=1}^{N} (x_j l_j) \text{---------------------} (8)$$

Parameters r_i and q_i are calculated as the sum of the group volume and area parameters R_k and $Q_k^{(13)\,6}$ $r_i = \sum \upsilon_k^{(i)} R_k$ and $qi = \sum \upsilon_k^{(i)} Q_k$

Where $\upsilon_k^{(i)}$ is the number of groups of type k in molecule i.

The residual part of the UNIQUAC equation is replaced by the solution-of-groups concept, and is given by eq (9)

In $\Upsilon_i^R = \sum \upsilon_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}]$ -----------(9) where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. The term $\Gamma_k^{(i)}$ is necessary to attain the normalization that activity coefficient y_i becomes unity as x_i -- 1. The activity coefficient for group k in molecule I depends on the molecule I in which k is situated..

The group activity coefficient Γ_k is found from eq (10)

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_{m=1}^{N} \theta_m \Psi_{mk} \right) - \sum_{m=1}^{N} \left(\theta_m \Psi_{km} / \sum_{n=1}^{N} \{ \theta_n \Psi_{nm} \} \right) \right] \text{----(10)}$$

The above also holds for ln $\Gamma_k^{(i)}$ in the above eq (10) θ_m is the area fraction of group m, and the sums are over all different groups and is given by

$\theta_m = Q_m X_m / \Sigma(Q_m X_m)$----- Where X_m is the mole fraction of groups m in the mixture. Group interaction parameter Ψ_{mn} is given by

$$\Psi_{mn} = \exp - [(U_{mn} - U_{nn}) / RT] = \exp - (a_{mn} / T) \text{ ------------------- (3.10)}$$

where U_{mn} is the measure of the energy interaction between groups m and n. Also a_{mn} and a_{nm} (two parameters per binary mixture of groups) are the parameters which must be evaluated from experimental phase equilibrium data. The functional groups considered and the R and Q values are given by Frendslund A. and Prausnitz J. M. [138] . A comprehensive list of the interactions parameters are given by prausnitz et. Al. [139] .The interaction parameters between the groups can be done by regression of either VLE or LLE data. The details of which are given in chapter 2 on literature surveys.

3.1.5 NRTL Method [140]

The activity coefficient equations are as follows

$$\text{In } \gamma_1 = X_2^2 \left[\lambda_{21} \left(\frac{G_{21}}{X_1 + X_2 G_{21}} \right)^2 + \frac{\lambda_{12} G_{12}}{(X_2 + X_1 G_{12})^2} \right] \quad \text{.. 11. (i)}$$

$$\text{In } \gamma_2 = X_1^2 \left[\lambda_{12} \left(\frac{G_{12}}{X_2 + X_1 G_{12}} \right)^2 + \frac{\lambda 12 \ G12}{(X_1 + X_2 G_{21})^2} \right] \quad \text{. .11. (ii)}$$

Where $G_{12} = \exp(-\alpha_{12} \lambda_{12})$ ...12(i)

$G_{21} = \exp(-\alpha_{12} \lambda_{21})$ ...12(ii)

The infinite dilution activity coefficient are related to the constants as follows

$\ln\gamma_1^{\infty} = \lambda_{12} + \lambda_{12} G_{12}$ ...13(i)

$\ln\gamma_2^{\infty} = \lambda_{12} + \lambda_{21} G_{21}$ ...13(ii)

Renon – and Prausnits[11] indicate that for non-electrolyte organic and non electrolyte mixtures $\propto_{12} = 0.3$ and for non electrolyte organic water system $\propto_{12} = 0.3$, for system under consideration have the value of $\propto_{12} = 0.30$.

3.1.6 THE NONRANDOM TWO-LIQUID EQUATION (NRTL):

The basic idea used in the derivations of the Wilson's equation is also used by Renon[141] in his derivation of the NRTL equation: however, Renon's equation unlike Wilson's is applicable to partially miscible as well ass completely miscible systems, which is a major improvement.

To define the local composition, Scoott's [142] two liquid theory of binary mixtures is used. If attention is focused on a central molecules of type 1. the probability of finding a molecule of type 2, relative to finding a molecule of type 1 about this central molecule is expressed in terms of the overall mole fractions and the Boltzmann factors

$x_{21} = x_2 \exp(-\alpha_{12} g_{21}/RT)$ ---------------- ---(14)

$x_{11}\ x_1 \exp(-\alpha_{12} g_{11}/RT)$-------------------------- (15)

And the probability of finding a molecule of type 1 about a central molecule of type 2 is given by

$x_{12} = x_1 \exp(-\alpha_{12} g_{12}/RT)$--------------------------------------- (16)

$x_{21} = x_2 \exp(-\alpha_{12} g_{22}/RT)$--------------------------------------- (17)

Where a_{12} is a constant characteristic of the nonrandom ness of the mixture

X_{ij} is the local mole fraction of molecule I in the immediate neighbourhood of molecule j

G_{ij} is the energy of interaction between an i-j pair of molecules

The local mole fractions are related by

$x_{21} + x_{11} = 1$-- ---(18)

$x_{12} + x_{22} = 1$-- ---(19)

Comparison of the assumptions in this theory with that of the quasichemical theory shows that α_{12} is the substitute of $1/z$ where z is the lattice coordination number details of which are given by Renon H. and Prausnitz J.M. [11]. Since z is in the order of 6 to 12, α_{12} is of the order of 0.1 to 0.3 (independent of temperature)

From eq (16) and (18), we obtain for the local mole fraction .

$x_{21} = x_2 \exp(-\alpha_{12}(g_{21} - g_{11})/RT) \ / \ x_1 + x_2 \exp(-\alpha_{12}(g_{21} - g_{11})/RT)$ --(20) and similarly form eq (3.24) and (3.26)

$x_{12} = x_1 \exp(-\alpha_{12}(g_{12} - g_{22})/RT) \ / \ x_1 + x_2 \exp(-\alpha_{12}(g_{12} - g_{22})/RT)$- (21)

The above eq (20) and (21) are introduced into the two liquid theory of scott which assumes that there are two types of cells in a binary mixtures one for molecule 1 and one for molecule 2 For cells containing molecules 1 at their center the residual gibbs energy (i.e. compared with ideal gas at the same pressure, temperature and composition) is the sum of all the residual gibbs energies for two body interactions experienced by the centre molecule 1 and is given by

$g^{(1)} = x_{11} g_{11} + x_{21} g_{21}$ ---------- (22)

If we consider pure liquid 1, $x_{11} = 1$ and $x_{21} = 0$, in this case the residual gibbs energy is given by

$g^{(1)}_{pure} = g_{11}$ ---------- (23)

Similarly for a cell containing molecule 2 at its center

$g^{(2)} = x_{12} g_{12} + x_{22} g_{22}$ ---------- (24)

$g^{(2)}_{pure} = g_{22}$ ---------- (25)

The molar excess Gibbs energy for a binary solution is the sum of two changes in residual gibbs energy first that of transferring x_1 molecules from a cell of the pure liquid 1 into a cell 1 of the solution, $(g^{(1)} - g^{(1)}_{pure})\, x_1$ and that of transferring x_2 molecules from a cell of pure liquid 2 into a cell 2 of solution, $(g^{(2)} - g^{(2)}_{pure})\, x_2$. Therefore

$g^E = x_1 (g^{(1)} - g^{(1)}_{pure}) + x_2 (g^{(2)} - g^{(2)}_{pure})$ ----------(26)

After appropriate substitution in equation-26 , one arrives at final equation-(27).

$g^E = x_1 x_{21} (g_{21} - g_{11}) + x_2 x_{12} (g_{12} - g_{22})$------------------------------------.(27)

Further,the following notation is introduced.

$T_{21} = (g_{12} - g_{22}) / RT$ and $G_{21} = \exp(-\alpha T_{21})$------------------------(28)

$T_{12} = (g_{21} - g_{11}) / RT$ and $G_{12} = \exp(-\alpha T_{12})$--------------------(29)

Notng that $g_{12} = g_{21}$. the equation for g^E becomes

$g^E / RT = x_1 x_2 (T_{21} G_{21} / x_1 + x_2 G_{21} + T_{12} G_{12} / x_2 + x_1 G_{12})$ --------(30)

The activity coefficients for the NRTL equations are found by diffrenciation of the above eq (3.36), the results of which are given below

In $y_1 = x_2^2 (T_{21} G^2_{21} / (x_1 + x_2 G_{21})^2 + T_{12} G_{12} / (x_2 + x_1 G_{12})^2)$ --------(31)

In $y_1 = x_1^2 (T_{12} G^2_{12} / (x_2 + x_1 G_{12})^2 + T_{21} G_{21} / (x_1 + x_2 G_{21})^2)$ --------(32)

For multicomponent mixtures the NRTL equation are readily generalized to solutions containing any number of components. In multicomponent mixture the excess gibbs energy is given by equation-(33)

$$g E / RT = \sum_{i=1}^{N} x_i \frac{\sum_{j=1} T_{ji} G_{ji} x_j}{\sum_{k=1} G_{ki} x_k} \quad \text{--------(33)}$$

where N is no of components and

$T_{ji} = (g_{ji} - g_{ii}) / RT$ $G_{ji} = \exp (- \alpha_{ji} T_{ji})$

The activity coefficients obtained after diffrenciation are

$$\text{In } Y_i = \frac{\sum_{j=1}^{N} T_{ji} G_{ji} x_j}{\sum_{k=1} G_{ki} x_k} + \sum_{j=1}^{N} \frac{x_j G_{ij}}{\sum_{k=1} G_{kj} x_k} \left(T_{ji} - \frac{\sum_{l=1}^{N} x_l T_{lj} G_{lj}}{\sum_{k=1} G_{kj} x_k} \right) \text{(34)}$$

The value of the nonrandomness parameter α is chosen depending on the type of system under consideration.

Type 1 includes those systems where deviations from ideality are not large, although they may be positive or negative. Type 1a systems includes most mixtures of nonpolar substances such as hydrocarbons and carbon tetrachloride but mixtures of hydrocarbons and paraffins are excluded. Type 1b systems includes some mixtures of nonpolar and polar nonassociated liquids while type 1c systems includes some mixtures of polar liquids with negative excess Gibbs energy. The recommended value of α is 0.3

Type 2 systems include mixture of saturated hydrocarbons with polar nonassociated liquids, the recommended value of a α is 0.2.

Type 3 systems include mixture of saturated hydrocarbons and the homolog perfluorocarbons, the recommended value of α is 0.4.

Type 4 systems include mixtures of strongly self-associating substances like alcohol with a nonpolar substance like an hydrocarbon or carbon tetrachloride, the recommended value of α is 0.40 to 0.55.

Type 5 is represented by two systems of polar substances (acetonitrile and nitromethane) with carbon tetrachloride, the recommended value of α is 0.47.

Type 6 is represented by two systems of water plus a polar, nonassociated substance (acetone and dioxane), the recommended value of α is 0.3.

Type 7 is represented by two systems of water plus a polar, selfassociated substance (butylglycol and pyridine), the recommened value of α is 0.47.

3.1.7 UNIVERSAL QUASI CHEMICAL THEORY (UNIQUAC)

It is postulated that liquids can be represented by a three dimensional lattice of equispaced lattice sites. The volume in the immediate vicinity of a site is called a cell. Each molecule of the liquid is considered to be divided into attached segments such that each segment occupies one cell. The number of cells is equal to the total number of segments (the assumption is that all cells are occupied i.e. there are no holes).

The partition function is given by $Z = Z_{\text{lattice}} Z_{\text{cell}}$

Where Z lattice refers to the situation where the center of every segment and the lattice sites coincide and Z cell provides for the contribution to z which are caused by the motion of segments about this central position and is assumed independent of composition. For a binary mixture containing N_1 molecules of component 1 and N_2 molecules of component 2 the Helmholtz energy of mixing is given by $\Delta A = -kT \ln Z_{\text{lattice}} (N_1, N_2) / Z_{\text{lattice}} (N_1, O) Z_{\text{lattice}} (O, N_2)$

Where k is the Boltzmann's constant and z is the configurational partition function. The molar excess Gibbs free energy is given by

$g^E = a^E = \Delta A / (n_1 + n_2) - RT (x_1 \ln x_1 + x_2 \ln x_2)$ (35)

Where R is the gas constant, x is the mole fraction and n is the number of moles.Following Guggenheim the lattice partition function is given by

$Z_{\text{lattice}} = \sum w(\theta) \exp[-U_o(\theta) / kT]$

Where w is the combinatiorial factor (number of ways in which the molecules can be arranged in space), and U_o is the potential energy of the lattice (it closely resembles the energy of isothermal vaporization from the liquid to the ideal gas state). Here w and U_o depend on the molecular configuration of the mixture designated by the variable θ which are permitted within the constraints of overall stichiometry.

A molecule of component 1 is represented by a set of bonded segments occupying r_1 lattice points. All segments are of nearly identical size but they differ in external contact area.For exmple in normal pentane the two methyl groups have a higher contact area than the two methylene groups, in neo-pentane the central carbon atom has no external contact area. For a molecule of component 1, the number of external nearest neighbours is given by zq_1, where z is the co-ordination number of the lattice and q_1 is the parameter proportional to the molecules external surface. Similarly for a molecule of type 2, the structural parameters are r_2 and q_2.Now attention is focused on the composition of a region in the immediate vicinity of a molecular 1. The local area fraction θ_{21} is the fraction of external sites around molecule 1 which are occupied by segments of molecule 2. similarly θ_{11}, θ_{22} and θ_{21} are defined.$\theta_{11} + \theta_{21} = 1$ $\theta_{12} + \theta_{22} = 1$ The following relation exits between q, z and r $½ (r - q) = r - 1$The definition of the structural parameters r and q is as follows $r_i = V_{wi} / V_{ws}$ And $q_i = A_{wi} / A_{ws}$Where V_{wi} and A_{wi} are the van der walls volume and surface of a segment of type i and V_{ws} and A_{ws} are the van der walls volume and surface of a standard segment. The choice of standard segment is arbitary e.g. methylene is the standard segment in a polymethylene chain. The volume and surface of the standard sphere is given by $V_{ws} = 4/3\ R^3_{ws}$ and$A_{ws} = 4\ R^2_{ws}$We obtain

$R_{ws} = 10.95 \times 10^5$ cm / mole, $V_{ws} = 15.17$ cm^3 / mole and $A_{ws} = 2.5 \times 10^9$ cm^2 / mole.The derivation of the expression for the lattice energy u is given by Abrams D. and Prausnitz J. M.. (1975)[143] as also the derivation for the combinatorial factor. The final results obtained are for a multicomponent mixture$g^E = g^E$ (combinatorial) + g^E (residual)

$$g^E (\text{comb}) / RT = \sum x_i \ln (\varnothing i / x_i) + z/2 \sum (q_i x_i \ln (\theta_i / \varnothing_i)) \qquad (36)$$

and

$$g^E (\text{res}) / RT = - \sum q_i x_i \ln (\sum \{\theta_j T_{ji}\}) \qquad (37)$$

where $T_{ji} = \exp \{ - [u_{ji} - u_{ii}] / RT \}$

and the activity coefficient for component i becomes

$$\ln y_i = \ln (\varnothing_i / x_i) + z/2\ qi \ln (\theta_i / \varnothing_i) + l_i - \theta_i / x_i \sum (x_j l_j) - q_i \ln \sum (\theta_j T_{ji}) + q_i - q_i \sum (\theta_j T_{ij} / \sum (\theta_k T_{kj})) \qquad (38)$$

where $l_j = z/2 (r_j - q_j) - (r_j - 1)$ (39)

and where the average area fraction θ and the average segment fraction $\varnothing$ are defined by

$$\theta = q_i x_i / \sum (q_j x_j) \; \varnothing = r_i x_i / \sum (r_j x_j) \qquad (40)$$

A simple derivation based on the two-liquid theory for the UNIQUAC model is given by Maurer [144], which avoids the inconsistencies which arise when a lattice one-fluid theory is used to derive the UNIQUAC equation. The essential step in Maurer's derivation is the adoption of Wilson's assumption that local composition can be related to overall compositions through Boltzmann's factors.

For describing the excess properties of alcohols in unassociated active components, an associated solution theory based on the UNIQUAC equation is developed by Nagata I. and Kawamura Y. [145], Nagata I. [146, 147] etc.

3.2.0 Theoretical considerations for Liquid-Liquid extraction in packed column

3.2.1 Holdup of the dispersed phase:

The initial investigations of the hold-up in packed columns are that of Appeal and Elgin [98]. However, no attempt was made to give any theoretical explanation of the curves obtained.

The following equation was proposed by Gayler and Pratt[99] based on the theoretical reasoning. This equation correlates hold-up below flooding point with phase flow rates and a characteristic velocity $\overline{V}_o$ characterizing, the packing and liquid-liquid system employed. No correlation was suggested for the evaluation of $\overline{V}_o$.

$$X = \frac{Vd}{\left(\varepsilon.\overline{V}o.-Vc/\ Y \right)} \qquad \text{where} \qquad (41)$$

Vd=dispersed phase superfacial velocity.

Vc=continuous phase superfacial velocity

Y=fractional free surface area of column used by continuous phase

$\overline{V}_o$ =characteristic velocity

Equation (42) was obtained by the same investigators[100,133] where $\overline{V}_a$ can be obtained as the slope of the straight line plot of

$$\left[V_d+\left(\frac{X}{1-X}\right)V_c\right] \text{Vs. } X(1\text{-}X)$$

$$\left[V_d+\left(\frac{X}{1-X}\right)V_e\right] = \varepsilon\ \overline{V}o\, X(1\text{-}X) \qquad (42)$$

Gayler and Pratt[22] have proposed the following correlation for 43(a) the estimation of the 'characteristic velocity'.

$$\frac{V_0\ \mu_0}{\gamma}=C\left(\frac{\Delta\ p\ \gamma^3}{\mu_c\ \mu_d}\right)^{0.5}\left(\frac{p_0}{\Delta_p}\right)^{-0.6}\left(\frac{a_t\ \mu_c{}^2}{\varepsilon\Delta\ p\ \gamma}\right)^{-0.4}\left(\frac{\varepsilon}{a_t\ d_T}\right)^{0.26} \text{ ----- } 43(a)$$

where,

γ=interfacial tension,

μ_c μ_d =viscosi of continuous phase and dispersed phase respectively.

ε=fractional voidage of column

a_t=surface area of packing per unit volume

.dT=tower diameter.

The value of $\overline{V}$o can also be obtained by Laaddha's correlation[149] given by following equation 43 (b):.

$$e\overline{V}_o=\frac{C}{\left[\frac{ap}{e^3g}\frac{sc}{\Delta p}\right]^{\frac{1}{2}}} \qquad 43(b)$$

where

C has the value of 4.9 and 6 for Raschig ring and Berl saddles, respectively.

a_t=surface area of packing per unit volume

ρc=Density of continuous phase

ρd= Density of dispersed phase

ε=fractional voidage of column

Δ ρ =ρc- ρd=Differewnce of Density of continuous phase and Density of dispersed phase

Sitaramayya and Laddha [101] tried to replace the characteristic velocity V_o in terms of the packing characteristic, and physical property of the system. Equations for $\frac{1}{\text{Vo}}$ which are proposed by Laddha showed 10.97% average deviation. Equation 44 (a) is then a generalized

correlation for the hold-up below flooding velocity.

$$\left[\frac{V_a}{V_c} + \frac{X}{1-X}\right]\left[\frac{C_c^{2}\, a_t}{g\,\varepsilon^{3}}\,\frac{p_c}{\Delta_p}\right]^{0.5} = 0.683 \quad x\,(1-X) \text{ --44 (a)}$$

where,

X=fractional hold up of dispersed phase

ρc=Density of continuous phase

g=gravitational constant.

Equation 44 (b) was proposed by Johnson and Laverng [102] where A', B' and n are constants.

$$\left[\frac{X}{V_d^{\,1.5}}\right] = A'\left[\frac{V_c^{\,n}}{V_d^{\,1.5}}\right]\left[\frac{X}{1-X}\right]^{3} + B' \text{ ----44 (b)}$$

For very high density difference systems like mercury and water, Watson and McNeese [116] attempted to correlate the hold-up of dispersed phase by equation (45) in terms of a 'slip velocity'.

$$[V_s]\,\frac{V_d}{X} + \frac{V_c}{1-X} \text{ ------(45)}$$

For Raschig rings and cylindrical packings a reliable correlation for prediction of slip velocity is available.

Burdett, et at [103] deviced a new technique for measurement of static and dynamic hold-up. But the restriction of similar refractive index of liquids and packing is so stringent that the usefulness of the method for general purpose is doubtful.

3.2.2 Holdup of the dispersed phase at flooding.

Gayler and Pratt [100] suggested equation (46) for estimation of hold-up at flooding.

$$X_1 = C_d \left[\frac{V_d^2\, a_t}{g\,\varepsilon^3}\right]\left[\frac{p_d}{\Delta_p}\right]^{0.25} \quad \text{----(46)}$$

Venkatraman and Laddha[150] modified the above equation by changing the exponent to 0.11 and the proportionality constant by 0.753 instead of 0.25 and 0.62, respectively as suggested by Gayler and Pratt. The equation suggested by Venkatraman and Laddha is as follows:

where

Cd=constant of dispersed phase.

Vd=dispersed phase superfacial velocity

a_t=surface area of packing per unit volume

ρd= Density of dispersed phase

ε=fractional voidage of column

Δ ρ =ρc- ρd=Difference of Density of continuous phase and Density of dispersed phase

g=gravitational constant.

$$X_1 = 0.753 \left[\left(\frac{V_d^2\, a_t}{g\,\varepsilon^3}\right)\left[\frac{p_d}{\Delta_p}\right]^{0.11}\right] \quad \text{---(47)}$$

The average deviation shown is 15.7% and the maximum deviation is ± 36%.

In a subsequent modification Chandra Shekharan and Laddha [104] obtained the equation (48) where C and n are constants.

$$X_1 = (1 - X_t)^{0.5} = C\left[\left(\frac{V_d^2\, a_t}{g\,\varepsilon^3}\right)\left[\frac{p_d}{\Delta_p}\right]\right]^n \quad \text{-----(48)}$$

The values of these constants for various types and size of packing are also reported by the authors.

In all the above equations an attempt was made to replace $\overline{V}$o or characteristic velocity term by the variables, characterizing packing and the system properties.

Also, these equations are obtained under the conditions of no mass transfer between the contacted phases. This transfer of solute between phases has the strong influence on hold-up and flooding. This happens due to increase in local turbulence and changes in surface tension values.

3.2.3 Holdup of the dispersed phase under solute transfer conditions:

Gayler and Pratt [105] correlated their data with equation (42). Degaleesan and Laddha[30]obtained the following transfer from continuous to dispersed phase (c-d) , and for solute transfer from dispersed phase to the continuous phase (d-c). Equations (49) and (50) give the estimation of hold-up of the dispersed phase,

$$\left[\frac{V_d}{V_c}+\frac{X}{1-X}\right]\left[\frac{V_c^{\,2}a_t}{g\varepsilon^3}\frac{p_c}{\Delta p}\right]^{0.5}=0.637\,X(1-X) \qquad (49)$$

$$\left[\frac{V_d}{V_c}+\frac{X}{1-X}\right]\left[\frac{V_c^{\,2}a_t}{g\varepsilon^3}\frac{p_c}{\Delta p}\right]^{0.5}=0.82X(1-X) \qquad (50)$$

$\Delta\rho=\rho c-\rho d$=Differewnce of Density of continuous phase and Density of dispersed phase

3.2.4 Correlations for maximum through put :

In the succeeding paragraphs, the correlations available for the flooding velocities of dispersed and continuous phases are discussed.

Blanding and Elgin[107]presented their results as the plot of square root of continuous phase flow rates against that of the dispersed phase.

Equation (51) was proposed by Breckenfeld and Wilke [108] in terms of packing characteristic and physical properties (especially the surface tension) of the system. Data of Elgin and of Wilke show 5% average deviation and maximum deviation of about 20%.

$$\frac{V_c\gamma^{0.24}\ \mu c^{0.33}\left(at\right)^{0.8}}{\Delta p\varepsilon^2}=\frac{3980}{\left(1+L^{0.5}\right)^2} \qquad (51)$$

where,

Vc=velocity of continuous phase.

a_t=surface area of packing per unit volume

L=ratio of dispersed phase to continuous phase velocity.

μ_c =viscosity of continuous phase

Row, Koffolt and Withrow [109] represented their data in the form of flooding curves graphically.

Bailard and Piret [110]defined the flooding in more precise way and presented an entirely different correlation (52) when dispersed phase does not wet the packing. A separate correlation (not obtained) would be necessary if dispersed phase preferentially wets packing.

$$0.55\left(\frac{g^{0.275}\Delta p^{0.465}}{(V)^{0.5}(P)^{0.3}(P_\infty)^{0.115}(\pi_\infty)^{0.05}}\right)\left(\frac{\varepsilon}{(d)_s^{0.65}}\right)^{0.5} X\left(\frac{6_{us}+6_{gd}}{6_{u8}}\right)^{0.2}=1.70+\left(\frac{V_\omega}{V_s^s}\right)^{0.5}\left(\frac{P_\omega}{P}\right)^{0.3} \qquad (52)$$

where

σ=surface tension

Vs=slip velocity.

ρ =density

Equation (53) is a more simple one to handle than equation (52), but is similar to it. Extensive variation in column sixe (up to 150 mm dia) and packing size and type was done. Dell and Pratt [35] who proposed the correlation also took into account the data of previous investigators. Values of constant C_2 are available for different packing types and sizes.

$$1 + 0.835\left(\frac{P_d}{P_c}\right)^{0.25}\left(\frac{V_d}{V_c}\right)^{0.5} = C_2\left[\left(\frac{V_c{}^2 a_t}{gE^3}\right)\left(\frac{Pe}{\Delta p}\right)\gamma e^{0.25}\right]^{-0.25} \qquad (53)$$

Crawford and Wilke [36] first time used large packings and columns [(12.5 mm to 37.5 mm) carbon Raschig rings and 300 mm dia column)] under the specified conditions, the flooding data were correlated by equations (54). The above correlations are similar to those proposed by Breckenfeld and Wilke[108]. Comparison of the two correlations shows that for geometrically similar systems similar conditions of hydrodynamics prevails.

$$(V_c{}^{0.5} + V_d{}^{0.5})^2 = \left(\frac{147000_{\Delta P}{}^{1.33}{}_{E}{}^{2}}{{}_{pc}{}^{0\Pi3}\, at\, {}_{pc}{}^{0.33}}\right) \text{ for } p_c \left[\frac{\left(V_c{}^{0.5} + V_d{}^{0.5}\right)^2}{a_t p_c}\right] < 50 \text{ and}$$

$$(V_c{}^{0.5} + V_d{}^{0.5})^2 = \left(\frac{198000_{\Delta P}\,{}_{E}{}^{1.5}}{{}_{pc}{}^{0.8}(at)^{0.5}\gamma^{0.2}}\right) \text{ for } p_c \left[\frac{\left(V_c{}^{0.5} + V_d{}^{0.5}\right)^2}{a_t p_c}\right] > 50 \qquad (54)$$

Treybal [152] modified the equation of Hoffing and Lockhart [38] and expressed Vc as a function of packing characteristic and physical properties of the systems [equation (55)]. Constant C of the equation can be evaluated by the equations given by Treybal. These equations give average deviations of nearly 10% in flooding velocities.

$$V_c = \frac{C\Delta_P{}^{0.625}\left(at/\ e^{0.12}\right)^{-0.838}}{pd^{0.275}pd^{0.1}pc^{0.125}pc^{0.125}\left(\frac{6_{us}}{6_{ua}}\right)^{0.625}} \qquad (55)$$

σ=surface tension

σcr=critical surface tension

ε=fractional voidage of column

Gayler and Pratt [100] proposed graphical correlations for flooding velocities in the form of Y against Z plots where

$$Y = \frac{\overline{V}_a}{V_t}[\,1 - \exp(-7.2\,dt)]\text{and } Z = \frac{{}_{\Delta p}\overline{gS}}{{}_{p\Delta}V_t{}^{2}}$$

Vt=terminal velocity.

$\Delta\rho$ =Difference of Density

γ=interfacial tension,

In the above equation, $\overline{S}$=0.38 d_v-0.92 $(\gamma/\ \Delta pg)^{0.5}$.

For the calculation of limiting flow rate they have selected transition point (below which hold – up varies linearly with dispersed phase superfacial velocity) as the criterion of flooding.

Sakiadis and Johnson[114]modified the correlation proposed by Dell and Pratt[111] [equation (53)] by adding a viscosity term to it and modified the constant C2 by accounting for packing characteristic, fractional voids and surface tension effect. Equation (56) was given as the, flooding correlation, where constant C'p can be evaluated by empirical equations.(56-a) and (56-b)

$$1+0.835\left(\frac{p_d}{P_c}\right)^{0.25}\left(\frac{V_d}{V_c}\right)^{0.5}=C\left[\left(\frac{C_{c^2}\ a_t}{ge^3}\right)\left(\frac{p_c}{\Delta_p}\right)\mu_c 0.25\ \lambda\ 0.25\right]^{-0.25} \quad \text{---(56)}$$

$$C_p\ \frac{0.87\ e^{0.0068}}{a_t^{\ 0.043}\ \gamma^{0.16}}\ \textit{for Raschig rings}\ .(56\text{-a})$$

And $C_p\ \frac{1.2\ e^{0.78}}{a_t^{\ 0.035}\ \gamma^{1/6}}$ *for Berlsaddles* (56-b)

It is claimed that the relation, that is, equation (56), is useful even for gas-liquid systems.

Venkatraman and Laddha[150]based on Dell and Pratt[111]analysis, applied dimensional analysis to this problem and obtained equation (57) where constants C and n are reported for different packing types. Average deviations in the range of 3% to 8% are claimed for different packings. It seems that introduction of the modified Weber group $(a_t e y)(pcVc^2)$ converges the data of various investigators.

$$\left[1+0.835\left(\frac{P_d}{P_c}\right)^{0.25}\left(\frac{V_d}{V_c}\right)\right]^{0.5}\times\left[\left(\frac{V_d^{\ 2}\ a_t}{g\ \varepsilon^3}\right)^{0.25}\left(\frac{P_c}{\Delta_p}\right)\right]^{0.25}=C\left[\frac{a_t\ \varepsilon\gamma}{P_c\ V_c^{\ 2}}\right] \quad \text{--(57)}$$

Numunaitis, et al [115] suggested that the group (a_t/e) which appears in the Crowford and Wilke correlation is not the representative of the capacities of the packings, other than

Raschig rings. They replaced this group by a packing factor which empiricakky accounts for the high capacity of the intelox saddles and Pall rings. These packing factors are given by following equations.

$$F_p = C_1 \,(a_t \,/\, \varepsilon)^3 \text{ And } F_p = C_2 \,(a_t \,/\, \varepsilon)^{1.37}$$

Where C_1 and C_2 are specified for different types of packings. In terms of these packing factors, Numunaitis. Ct al suggested a graphical correlation using

$$\frac{(V_c^{\,0.5} + V_c^{\,0.5})^2 \, p_c}{a_t \, \mu_c} \text{ as ordinate and} \left(\frac{\mu_c}{\Delta_p}\right)(F_p \, \varepsilon^2)^{1.5} \left(\frac{\gamma}{P_c}\right)^{0.2} \text{ as abscissa.}$$

Watson and McNeese [116] studied the hydrodynamics of counter-current flow of high density difference fluids such as mercury and water. They suggested a correlation based on the assumption of constant superfacial slip velocity. But this correlation does not apply over a wide range of fluid properties. In a later development[96] they covered the wide range of fluid properties (but covering only Raschig rings as the packing material). Equation (58) represents the correlation, as suggested by the authors.

$$[V_c^{\,0.5} + \{0.844\,\Delta_p^{\,0.298}\,\mu_c - {}^{0.084}\,\varepsilon^{-0.078}\}\,V_c^{\,0.5}] \qquad \text{--(58)}$$

$$= 23.8\left(\frac{\Delta_p^{\,0.269}\, d_p^{\,0.494}\, \varepsilon^{0.5}}{\mu_c^{\,0.084}}\right)$$

where dp=packing size., other symbols have conventional meaning already cited.

3.2.5 Mass transfer studies in packed column:-

For the estimation of height of the packed column required for the desired separation, an understanding of the mechanisms of mass transfer is essential. Many attempts have been made to understand the mechanism of mass transfer. This also helps in predicting the mass transfer rates accurately. Among many factors which govern the rate of mass transfer are, haydrodynamics of the phases in contact, interfacial area, packing characteristic and physicochemical properties of the system. The equations (59-a) and (59-b) given below take into account these factors.

Gayler and Pratt[117] have proposed the equation (59-a) and (59-b) in which part (a) relates the area based dispersed phase mass transfer coefficient in terms of a characteristic Reynolds number R_c

Phase velocities, fractional viodage and hold up of the dispersed phase. Part (b) of the equation (59) is a similar correlation for the continuous phase mass transfer coefficient where $m + 0.45 - 0.2\, d_v$

$$\frac{K_d\ \varepsilon\ X^{1+m}}{V_d} = 6.4 \ x\ 10^{-5}\ R_{cd}^{\ 0.5} \left[1 + \frac{(V_c\ X)}{V_d\ (1-X)}\right]^{1.5} \text{----------- (59 a)}$$

$$\frac{K_d\ \varepsilon\ X^{1+m}}{V_d} = 5.3 \ x\ 10^{-5}\ R_{cd}^{\ 0.5} \times \left[1 + \frac{(V_c\ X)}{V_d\ (1-X)}\right]^{1.5} \text{----------- (59 b)}$$

where,

R_{cd} =characteristic Reynold number based on dispersed phase flow rate

R_{cc} = characteristic Reynold number based on continuous phase flow rate

Kd=Individual mass transfer coefficient based on dispersed phase flow rate

Kc= Individual mass transfer coefficient continuous phase

ε =fractional voidage of column

X=fractional hold up

Laddha and Smith[118] expressed their results, on mass transfer studies in terms of the height of transfer units. They found that $(HTU)_d$ is constant with the flow rates of the phases, in the range of flow rates covered by them.

Similar investigations were made by Gayler and Pratt[105] who presented the graphical correlations showing influence of flow velocities on the mass transfer coefficients.

Equation (60) was developed by Simth and Beckman [119] which correlated height of transfer units of continuous phase to that of dispersed phase.

$(HTU)_c + C_2 (V_c / V_d)^n$ (60)

$(HTU)_{c}$= height of transfer units of continuous phase

Krishnan, et al [120], extended the theoretical analysis of Handlos and Baron [121], Kroning and Brink [122] and proposed the equations (61) and (62). These equations are for individual phase volumetric mass transfer coefficient in terms of packing characteristics, hold up of the dispersed phase phase follow rates and physical properties (Schmidt's number) of the systems. The correlations proposed by Krishnan, et al [46] show 15% average deviations. The values of constant α are reported.

$$Kca = \alpha X (1-X)\left(\frac{a_t\, p_c}{\varepsilon^3 g \Delta_p}\right)^{-0.5}\left(1+700\frac{V_c^{0.5}}{\gamma}\right)^{-0.5}\left[1+\left(\frac{N_{scd}}{N_{scc}}\right)^{q}\right]^{-1}\left(\frac{\gamma}{\Delta_p\, g}\right) \quad (61)$$

$$Kda = \alpha' X (1-X)(a_t / \varepsilon^3 g)^{-0.5}\left(\frac{p_c}{\Delta_p}\right)^{-0.5}\left(\frac{\gamma}{\Delta_p g}\right)^{-0.5}$$

$$\left[1+700\left(\frac{V_c^{0.5}}{\gamma}\right)\right]^{-1}\left[1+\left(\frac{N_{scd}}{N_{scc}}\right)^{0.5} -\right]^{-1} \quad (62)$$

where,

α'=air

$\frac{N_{scd}}{N_{scc}}$= Schmidt number based on dispersed phase/ Schmidt number based on continuous phase

$Kc\ a$ = mass transfer coefficient based on continuous phase

$Kd\ a$ = mass transfer coefficient based on dispersed phase

γ=interfacial tension,

The estimation of overall mass transfer coefficient was first undertaken by Gayler and Pratt [105]. They compared the value of the overall mass transfer coefficients obtained experimentally with the values estimated from the calculation of individual phase mass transfer coefficient and adding them in the usual manner, to estimate the overall coefficient. Equation (59) was used for calculating individual phase mass transfer coefficients. They found that experimental values of the overall mass transfer coefficients are 50% to 200% greater than those predicted from individual coefficients. Since the deviations were large, no correlations for overall coefficients were suggested.

Laddha, et al [123] proposed, the equation (63) for the prediction of volumetric overall mass transfer coefficient based on the dispersed phase. They also tested the data of Leibson and Becjkman [50], which showed good agreement with equation (63).

$$Kod\ a = 0.014\ X\ (1-X)\ \left(\frac{a_t}{\varepsilon^3\ g}\right)^{-0.5} \left(\frac{P_c}{\Delta_p}\right)^{-0.5} \times$$

$$\left(\frac{\gamma}{\Delta_p\ g}\right)^{-0.5} \left(\frac{\mu_c\ \mu_d}{(\mu_p\ g)\ (m\ \mu_d + \mu_d}\right) \tag{63}$$

Kod a=Overall mass transfer coefficient based on dispersed phase

Koc a=Overall mass transfer coefficient based on continuous phase

ρd= Density based on dispersed phase

ρc= Density based on continuous phase

Δ ρ=Density difference

μ_d =Viscocity based on dispersed phase

μ_c =Viscocity based on continuous phase

Gopalrao and Ramamurty[124] obtained the area based overall mass transfer coefficient, K_{0C} [equation(24)] in terms of dispersed phase flow rate and characteristic droplet diameter d_{sv}. They found that K_{0C} was independent of the continuous phase flow rates.

$$\left[\frac{K_{bc}}{d_{cs}\ V_0}\right] = C\ [V_d{}^n] \tag{64}$$

Koc = Individual mass transfer coefficient based on continuous phase

dcs=characteristic droplet diameter.

3.2.6 Estimation of interfacial area in packed columns:

Pratt, et al [125] studied the droplet behaviour and found out that for the packings above critical size, the interfacial area per unit volume a is given by:

$$a = \frac{6\ \varepsilon\ X}{d_{vs}} \text{ --(65)}$$

Where d_{vs} is given by :

$$\left[\frac{d_{vs}^{2}\ \Delta_{p}\ g}{\gamma}\right]^{0.5} = \left[1 + 700\ \left(\frac{V_{c}\ \mu_{c}}{\gamma}\right)\right]$$

In a later modification of their own correlation Gayler and Pratt [126] suggested the following correlation.

$$a = \frac{6\ \varepsilon\ X}{d_{vs}} = \frac{6\ V_{d}}{d_{cs}^{0}\ V_{0}} \text{ --------------------------------------(66)}$$

Where d_{cs} is given by :

$$\frac{d_{vs}^{2}\ \Delta_{p}\ g}{\gamma} = 1.42\left(\frac{\Delta_{p}\ \gamma^{3}}{\mu_{c}^{4}\ g}\right)^{0.475}$$

and

$$d_{vs} = 0.92\left(\frac{\gamma}{\Delta_{p}\ g}\right)^{0.5}\left(\frac{V_{0}\ \varepsilon\ X}{V_{d}}\right)$$

Where $d_{vs}o$ is independent of column diameter and packing size. The characteristic velocity $\overline{Vo}$ can be obtained from the hold-up as discussed earlier.

In an entirely novel approach Puranik and Sharma [127] applied the theory of 'extraction with fast-Pseudo-first order reaction' to this problem. They found out that when

$\frac{D_K}{K_L^{2}} = > 10$ where,

D=Diffusivity of solute.

K=pseudo first order reaction rate.constant.

E=solubility of solute in the phase in which it is transfered

KL.=mass transfer coefficient in the phase in which reaction is taking place.

then the specific rate of extraction becomes independent of hydrodynamic factors. Thus,

$$a = \frac{R_a}{(E)(DK)^{0.5}} \qquad (67)$$

Where (R a) is the specific rate of extraction.

D=Diffusivity of solute.

K=pseudo first order reaction rate.constant.

E=solubility of solute in the phase in which it is transfered

In a recent development [128] it was shown that with kinetics of coalescence and breakage of droplets, it is possible to calculate the interfacial area of contact. Billet and mackowiak [129] studied the new types of columns called packed tube columns. Here the diameter of the packings is slightly less than the diameter of the column itself. Thus, the packings are regularly stacked in the tube column. Main advantage with such type of columns is that, systems with extreme differences of physical properties can successfully be separated, again throughput from such columns are high compared to packed column. Regularly stacked packing reduce axial mixing and thus higher efficiencies could be obtained.

Billet and Mackowiak[130] proposed following correlations for the flooding velocities.

$$F^*_{CFL} = 0.402\, e^{112} (X)^{0.5} \qquad (68)$$

Where flooding factor is given by

$$F^*_{CFL} = V_c\left(\frac{P_c}{\Delta_p}\right)\left(\frac{a_t}{g\ \varepsilon^3}\right)^{0.5} \times \left(\frac{V_d + V_c}{\gamma}\right)^{0.1}\left(\frac{\mu_c}{\mu_w}\right)^{0.3}$$

and flow parameter X is given by

$$X = \left(\frac{V_d}{V_c}\right)\left(\frac{P_4}{P_c}\right)^{0.5}$$

For the hold up of the dispersed phase they proposed following correlation [154]

$$X = \left(\frac{C_3}{\varepsilon}\right) We^{0.5} \qquad (69)$$

Where we is the modified Weber number given by

$$We = \left(\frac{p_d\ V_d^2}{\Delta_p\ g\ \gamma}\right)^{0.5}$$

where,

ρd= Density based on dispersed phase

Δ ρ=Density difference

Vd=Superfacial velocity of dispersed phase.

g=gravitational constant

γ=interfacial tension,

The performance of Sulger static mixers as packings has been investigated recently. The graphical correlations are proposed in terms of (HTU) against total column capacity. Throughput and separation capacity of the packings are claimed to be well so as to use them in commercial scale separations.

For a packing size greater than the critical size of packing, the characteristic drop diameter below the loading point is given by the following equation: - [106]

$$dp = 0.92\left(\frac{\sigma}{\Delta pg}\right)^{0.5}\left(\frac{\overline{U\circ_E x}}{Ud}\right) \qquad \ldots (70)$$

If the droplets are assumed to be of uniform size and spherical in shape, then the value of 'a' would be given by the following equation:-

$$a=\frac{6_E x}{dp} \qquad \ldots (71)$$

Equations (70) and (71) give

$$a=\frac{6Ud}{0.92\left(\frac{a}{\Delta P.g}\right)^{\frac{1}{2}} U0} \qquad \text{---} (72)$$

Where d_p = droplet size. cms.

U_O = characteristic droplet velocity, cm/sec.

x = fractional holdup of the dispersed phase.

$\in$ = fractional voidage of packing.

σ = interfacial tension of the system, dyno/ cm^2

$\Delta\rho = (\rho_C - \rho_d)$ or $\rho_d - \rho_C$

= density difference between the two phases, gm/cm^3.

a= interfacial area per unit volume of contactor,

3.2.7 Determination of(N.T.U.)o.d. and (N.T.U.)$_{O.C.}$:

It is well known that N.T.U.)$_{O.C.}$ and N.T.U.)$_{O.d.}$ could be calculated with the help of equations-(73) and (74) if the slope of the equilibrium line is not a constant. [40,131]

$$(N.T.U.)o.c. = \int \frac{dH_B}{H_B^* - H_{B1}} \qquad (73)$$

$$(N.T.U.)o.d.. = \int \frac{dHB}{H_{B1} - H'B^*} \qquad (74)$$

Where (N.T.U.)$_{O.C.}$ and (N.T.U.)o.d. = Number of transfer units based on continuous and dispersed phases respectively.

H_B = Concentration of solute in the extract phase expressed as gm. of solute per gm. of solvent in the extract phase.

H'_B = Concentration of solute in raffinate phase, expressed as gm. of solute per gm. of non-solute in the raffinate phase.

H^*_B and $H'_B{}^*$ = equations-(73) and (74) could be evaluated graphically. Knowing the total effective height of packing, the overall height of transfer unit could also be evaluated.

The values of N.T.U.$_{\text{o.d.}}$ and N.T.U.$_{\text{o.c.}}$ obtained graphically from the values of N.T.U.$_{\text{o.c.}}$ obtained.

3.2.8 Determination of HTUoc and HTUod & HTUc and HTUd

Overall Height of Transfer unit is determined by following equations:

HTUoc=118.5/NTUoc 75(a)

where

HTUoc=Z/NTUoc

HTUod=118.5/NTUod 75(b)

where

HTUod=Z/NTUod

Over all height of transfer unit continuous phase side (HTUoc) and height of transfer unit continuous side (HTUc) are related by the following equations.

HTU)oc=(HTU)c+(HTU)d(dHc/dHd)avg.Gc/Gd 75©

where HTU)oc= Over all height of transfer unit continuous side, cm

HTU)c= height of transfer unit continuous side, cm

HTU)d= height of transfer unit dispersed side, cm

Gc=mass flow rate of continuous phase., gm/cm^2. min

Gd=mass flow rate of dispersed phase., gm/cm^2. min

(dHc/dHD) = average slope of equilibrium curve

Overall height of transfer unit disersed side (HTU)od and height of transfer unit continuous side (HTU)d are related by following equation:-

HTU)od=(HTU)d+(HTU)c(dHd/dHc)avg..Gd/Gc 75(d)

where HTU)od= Over all height of transfer unit dispersed side, cm

HTU)d= height of transfer unit dispersed side, cm

Remaining symbols have the same meaning as in equation -75(c)

3.2.9 Determination of Koc.a and Kod.a and individual mass transfer coefficients (Kod, Koc):

Over all Mass transfer coefficient is determined by following equations.[131]

Koc.a=Vcavg/HTUoc 76(a)

where

Koc.a = (Vcavg*Z)/ (NTUoc)

K_{oc}.**a** = overall mass transfer coefficient based on continuous phase,

Kod.a =Vdavg/HTUod 76(b)

where

Kod.a =(Vdavg*Z)/ (NTUod)

K_{od} **.a** = overall volumetric mass transfer coefficient based on dispersed phase,

Individual Mass transfer coefficient is determined by following equations:

Koc =(Koc.a) / a 76(c)

where

Koc.=[Vcavg*Z/(NTUoc)] / a

Koc.=Individual Mass transfer coefficient based on continuous phase,

Kod =(Kod.a) / a 76(d)

where

Kod.=[Vdavg*Z/(NTUod)] / a

Kod.=Individual Mass transfer coefficient based on dispersed phase